Tetrahedron Letters No.28, pp. 2485-2488, 1970. Pergamon Press. Printed in Great Britain.

THE REACTION OF p,p'- DITOLYL SULFOXIDE WITH p-TOLYLLITHIUM EVIDENCE FOR AN ARYNE INTERMEDIATE

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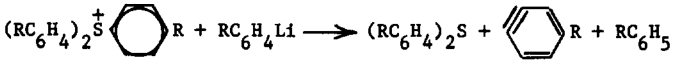
(Received in USA 24 April 1970; received in UK for publication 18 May 1970)

Several years ago, we reported on the reaction of diphenyl sulfoxide with phenyllithium which yielded diphenyl sulfide and diphenyl.[2] Formation of triphenylsulfonium cation (eq 1, R=H) as an intermediate was proposed on the basis of its ready synthesis from diphenyl sulfoxide and phenylmagnesium bromide.[3] The sulfonium cation was postulated to react with phenyllithium to give diphenyl sulfide and benzyne; the latter then went on to give diphenyl (eqs 2 and 3, R=H):

$$(RC_6H_4)_2S{=}O + RC_6H_4Li \longrightarrow (RC_6H_4)_3\,S^+ + LiO^- \qquad (1)$$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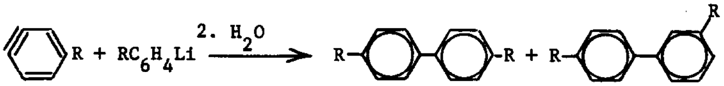
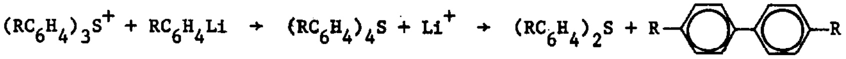
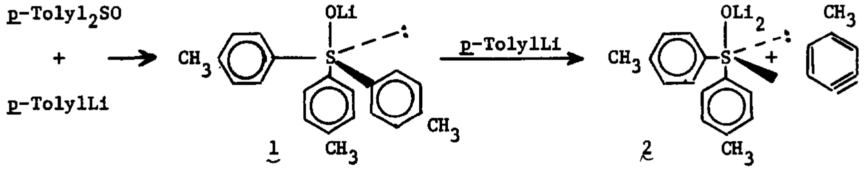

(3)

Franzen carried out the reaction of tri-o-anisylsulfonium cation with phenyllithium in ether at room temperature and above.[4] He proposed as the major pathway the formation of a tetracoordinate S(IV) intermediate[5], a tetraaryl sulfur, which collapsed to give the products. A similar intermediate had been proposed earlier by Wittig for the reaction of triphenylsulfonium cation with phenyllithium (eq 4, R=H) in ether.[10] Franzen considered the aryne pathway to be of minor importance. Recently, this reaction has been reinvestigated by Trost, LaRochelle, and Atkins[7] and by Khim and Oae.[11] Their results are not completely compatible with one another. Trost reported that the reaction of tri-p-tolylsulfonium cation with phenyllithium in tetrahydrofuran at -78° gave p,p'-ditolyl but no m,p'-ditolyl, while Oae reported the formation of both isomers in refluxing ether. An aryne


(4)

mechanism involving solely 4-methylbenzyne should have given a 50:50 mixture of both ditolyls.[12] Trost[7]concluded that no aryne was involved but only a tetraaryl sulfur intermediate of the sort originally postulated by Wittig. Oae postulated both the aryne and tetraaryl sulfur pathways.

We have investigated the reaction of *p*,*p*'-ditolyl sulfoxide and of tri-*p*-tolylsulfonium bromide with *p*-tolyllithium in ether at room temperature. From the sulfoxide, the products and yields were: *p*,*p*'-ditolyl sulfide, 66.1%; *p*,*p*'-ditolyl, 31.4%; *m*,*p*'-ditolyl, 25.6%. Assuming that all of the *m*,*p*'-isomer arises via an aryne pathway (eqs 1, 2, and 3, R=*p*CH_3), 81% of the *p*,*p*'-ditolyl should arise via an aryne and 19% via another route, perhaps via the tetraaryl sulfur (eq 4, R=*p*-CH_3). From the sulfonium salt in ether at room temperature, we obtained: *p*,*p*'-ditolyl sulfide, 86.8%; *p*,*p*'-ditolyl, 71.5%; *m*,*p*'-ditolyl, 5.1%. The sulfonium salt under our reaction conditions gave very little aryne. Therefore, it is hard to imagine it as the intermediate in a reaction which leads from *p*,*p*'-ditolyl sulfoxide to most of the *m*,*p*'-ditolyl. An alternative tetracoordinate S(IV) intermediate which reacts with p-tolyllithium to give 4-methylbenzyne is shown in eq 5. Aryne formation from **1** via intramolecular hydrogen abstraction or from the triphenylsulfonium salt via reaction with lithium oxide seem unlikely. Triarylsulfonium salts plus hydroxide ion give products which do not arise from aryne intermediates.[13] It appears that intermediate **1** reacts



(5)

mostly via an aryne route (eq 5) and partly via the sulfonium cation route; i.e., cleavage of the SO bond in **1** results in the sulfonium cation which reacts principally through the tetraaryl sulfur (eq4) to give products. A very small fraction of the sulfonium cation also reacts via an aryne route (eqs 2 and 3). The stereochemical structures of **1** and **2** are not known; the drawings are patterned after the structure of SF_4 which has a trigonal bipyramidal shape.[6] Intermediate **2** is the structure one might expect for an intermediate involved in substitution at dicoordinate S(II)[14] or for the reduction of a sulfoxide by two electron transfer from a metal or a cathode. A similar intermediate has been mentioned as a possibility by Sekera, Fauvet and Rumpf[15a] in the reaction of dialkyl sulfoxides with organomagnesium halides although they seem to prefer an alternative intermediate.[15b]

The reactions were carried out in diethyl ether at room temperature in nitrogen-flushed, serum-capped flasks. Excess, standardized[16] *p*-tolyllithium in ether was added by syringe. The *p*-tolyllithium[12] was prepared in centrifuge tubes from *n*-butyllithium and *p*-bromotoluene in benzene, washed several times with benzene with the aid of centrifuging, and dissolved in ether. The products were analyzed using glc on an Apeizon-L column with biphenyl as a standard.[17] Products were collected from the column and identified by ir spectral comparison with authentic samples. Small amounts of *p,p*'-ditolyl and *m,p*'-ditolyl in the *p*-tolyllithium solution were corrected for using quantitative glc techniques.

Our studies on the reaction of various sulfoxides with organolithium reagents are continuing.[18]

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5. The misnomer pentacoordinate has been used by some authors [6,7,8] to describe tetracoordinate sulfur(IV) species; the electron pair is considered to be a ligand.[6] While it has the virtue of distinguishing between $:SR_4$ and sulfones[7], it leads to confusion in other instances. For example, sulfoxides, which are usually considered tricoordinate, now become, by virtue of a nonbonding pair on sulfur, tetracoordinate, and so cannot be distinguished from sulfones. Carried to its logical extreme, $R_2\ddot{S}:$, $R\underset{..}{\ddot{S}}:^-$, and $:\underset{..}{\ddot{S}}:^=$, are all tetracoordinate. We prefer a less ambiguous nomenclature[9] in which the number of ligands define the coordination number and the valency or oxidation state is either written out or preferably enclosed in parentheses. The valency is defined as equal to the number of bonds to sulfur plus the formal charge on sulfur.
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18. This research was supported in part by a grant from the National Science Foundation, GP-8136.